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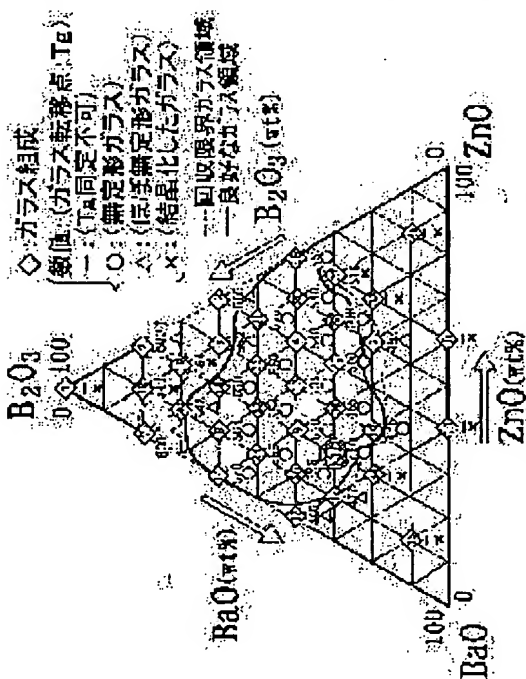
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(54) LEAD-FREE LOW-MELTING GLASS FOR SEALING



(57)Abstract:

PROBLEM TO BE SOLVED: To provide lead-free glass for sealing equivalent to PbO-B2O3 low-melting glass.

SOLUTION: The lead-free low-melting glass for sealing comprises a lead-free composition consisting of a network forming oxide, an intermediate oxide and a network modifying oxide, wherein a vitreous low-melting substance is selected by adjusting the weight % of these oxides. The lead-free composition is composed of B2O3 or V2O5 as the network forming oxides, ZnO as the intermediate oxide and BaO as the network modifying oxide, and adjusted to the range of 20-80 wt.% of B2O3, 0-60 wt.% of BaO and 0-60 wt.% of ZnO, or to the range of 30-70 wt.% of V2O5, 0-50 wt.% of ZnO and 50-80 wt.% of BaO.

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the closure of electronic parts especially a fluorescent indicator tube, and the low-melt point point nonlead glass for sealing processing of a semiconductor package.

[0002]

[Description of the Prior Art] Conventionally, sealing processings are a series of activities which are used in the field of the electronics industry, stop opening of a metal, glass, or a ceramic container, and prevent invasion of gas or moisture. In order that sealing may guarantee stable actuation of the electron tube or electronic parts, it is an indispensable activity, and the lead glass of the shape of powder containing current and lead oxide (PbO) is used. The glass of 2OPbO-B3 system with which the principal component of lead glass harnessed the low melting point nature of PbO and high solubility was a core.

[0003] However, the venenosity which lead has in recent years is posing a problem. It is said that it will commit the increment in a denaturation corpuscle, reduction of hemoglobin, and a brain center, and will produce Alzheimer's disease in a hematogenous enzyme failure and an erythrocyte if this lead is taken in by the body. Lead exists also in the usual environment widely, exists also in the body, is always taken in and excreted (80mg of body Nakahira **, 70kg), and its intake is abundant and it is poisoned when accumulated in the inside of the body. When the electronic parts which furthermore used lead glass as sealing material are discarded, lead permeates underground by acid rain and the harmful nature is regarded as questionable as it is what leads also to soil pollution and groundwater contamination. For this reason, atmospheric control has also been carried out with the regulation from the Occupational Safety and Health side which prevents an occupational disease.

[0004] The development of the glass for sealing of an owner lead system and the sealing glass of the unleaded system for which it can be substituted currently used for old various electronic parts from such a background is demanded.

[0005] The research report is made about TiO₂ system, 2OP5 system, etc. as unleaded system low melting glass until now, and it is shown clearly that what is low-melting can be prepared. However, low-fever expansion, an adhesive property, closure nature, and the sealing glass of the unleaded system which was further excellent in chemical durability have not yet escaped from the field of a fundamental research, so that it can substitute completely with owner lead system glass.

[0006]

[Problem(s) to be Solved by the Invention] This invention not only by the mere element permutation but by ingredient retrieval based on the physicochemical quality of the element which constitutes glass structure and it By the difference in the organization potency force of the glass by single bond reinforcement with oxygen, a metallic oxide A mesh formation oxide (Network former:NWF), an intermediate oxide (Intermediate), Paying attention to being classified with a mesh modifier oxide (Network modifier:NWM), the metallic oxide with nearest PbO and single bond reinforcement is ZnO, Since both PbO and ZnO have a similar function in the structure of glass as an oxide with the thing with almost equal (144 kcal/mol) dissociation energy and the number of oxygen coordination per mol, ZnO is used as an alternative oxide of PbO, and

it is [0007]. Furthermore, by using the oxide containing a metal with big atomic weight like BaO as the quality of an alternative of PbO, a role of a mesh modifier oxide which embellishes the network structure with the form where association of oxygen is cut in oxide system glass is made to play, and it aims at obtaining the glass for sealing which matched or was excellent in lead system low melting glass.

[0008]

[Means for Solving the Problem] In order to attain the above-mentioned purpose, this invention is a unleaded system constituent set to the 1st from a mesh formation oxide, an intermediate oxide, and a mesh modifier oxide. The unleaded low melting glass for sealing processing which prepares weight % of these oxides and comes to select the low-melt point point matter of glassiness, B-2 O₃ or V₂O₅, and an intermediate oxide to the 2nd ZnO, [a mesh formation oxide] The unleaded low melting glass for sealing processing given [above-mentioned] in the 1st invention from which the mesh modifier oxide constituted the unleaded system constituent by BaO, B-2 O₃ which constitutes the above-mentioned unleaded system constituent in the 3rd 20 - 80wt%, BaO - 60wt%, The unleaded low melting glass for sealing processing the above 1st which prepared ZnO in the range of 0 - 60wt% - given in the 2nd invention, BaO 30wt(s)% 50wt(s)%, [B-2 O₃ which constitutes the above-mentioned unleaded system constituent in the 4th] The unleaded low melting glass for sealing processing given in either the above 1st which ZnO prepared to 20wt(s)% - the 3rd invention, ZnO 30 - 70wt% 0 - 50wt%, [V₂O₅ which constitute the above-mentioned unleaded system constituent in the 5th] The above 1st whose BaO is 50 - 80wt%, or the unleaded low melting glass for sealing processing given in the 2nd invention, The unleaded low melting glass for sealing processing given in either the above 1st which carried out addition preparation of Bi₂O₃ to the above-mentioned unleaded system constituent the 6th - the 5th invention, Therefore, it is constituted by the unleaded low melting glass for sealing processing given in either the above 1st which carried out addition preparation of TeO₂ to the above-mentioned unleaded system constituent the 7th - the 5th invention, and the unleaded low melting glass for sealing processing given in either the above 1st which mixed the refractories filler to the 8th - the 7th invention.

[0009] Therefore, on the occasion of preparation of the low melting glass of a unleaded system, ZnO and BaO are chosen as a mesh formation oxide as B-2 O₃ or V₂O₅, and a mesh modifier oxide. Prepare the unleaded system low melting glass of this 3 component system, and structural analysis by the glass transition point, softening temperature, the coefficient of thermal expansion, and powder X-ray diffractometry (XRD) estimates the physicochemical property of the low melting glass of a unleaded system. While clarifying the role of the mesh modifier oxide in a mesh formation oxide, sealing of the prepared unleaded system low melting glass and a closure property can be checked, and the glass for sealing which is equal to the glass of 2OPbO-B3 system can be obtained.

[0010]

[Embodiment of the Invention] the oxide which can form the three-dimension mesh which an oxide with a mesh formation oxide (NWF), i.e., glass organization potency, makes, i.e., the oxide which can form the frame of glass (amorphous substance: amorphous), -- B-2s O₃ and V₂ -- they are O₅, SiO₂, and P₂O₅ grade.

[0011] An intermediate oxide, i.e., the oxide which replaces some mesh formation oxides (NWF), and joins mesh formation, and can also play a role of a mesh modifier oxide, is

ZnO, PbO, and aluminum2O3 grade, although glass cannot be formed if independent. [0012] Although glass formation cannot be performed in a mesh modifier oxide (NWM), i.e., independent, the oxides which can enter into the mesh which a mesh formation oxide (NWF) makes as one component of glass, and can affect a property are BaO, ZnO, PbO, etc.

[0013] B-2s O3, ZnO, and BaO were chosen from the above-mentioned physicochemical standpoint as a raw material metallic oxide, and the vitrification condition after baking was made to clarify, as the presentation (brewing schedule wt%, Charge g) shown in table 1B-1-B-32 is shown in Table 2.

[0014]

[Table 1]

組成	B ₂ O ₃		ZnO		BaO	
	仕込組成(wt%)	仕込量(g)	仕込組成(wt%)	仕込量(g)	仕込組成(wt%)	仕込量(g)
B-1	100	15.0	0	0	0	0
B-2	80	12.0	20	3.0	0	0
B-3	60	9.0	30	4.5	10	1.5
B-4	40	6.0	40	6.0	20	3.0
B-5	20	3.0	50	7.5	30	4.5
B-6	0	0	60	9.0	40	6.0
B-7	80	12.0	0	0	20	3.0
B-8	60	9.0	10	1.5	30	4.5
B-9	40	6.0	20	3.0	40	6.0
B-10	20	3.0	30	4.5	50	7.5
B-11	0	0	40	6.0	60	9.0
B-12	80	12.0	0	0	20	3.0
B-13	60	9.0	20	3.0	20	3.0
B-14	60	9.0	0	0	40	6.0
B-15	40	6.0	60	9.0	0	0
B-16	40	6.0	30	4.5	30	4.5
B-17	40	6.0	0	0	60	9.0
B-18	80	12.0	10	1.5	10	1.5
B-19	70	10.5	20	3.0	10	1.5
B-20	70	10.5	10	1.5	20	3.0
B-21	50	7.5	40	6.0	10	1.5
B-22	50	7.5	30	4.5	20	3.0
B-23	50	7.5	20	3.0	30	4.5
B-24	50	7.5	10	3.0	40	4.5
B-25	40	6.0	50	1.5	10	7.5
B-26	40	6.0	10	1.5	50	7.5
B-27	30	4.5	60	9.0	10	1.5
B-28	30	4.5	50	7.5	20	3.0
B-29	30	4.5	40	6.0	30	4.5
B-30	30	4.5	30	4.5	40	6.0
B-31	30	4.5	20	3.0	50	7.5
B-32	30	4.5	10	1.5	60	9.0

[0015]

[Table 2]

	理論量(g)	回収量(g)	ガラス収率(%)	回収率(%)	非溶融(%)	調製したガラスの外観
B-1	15.0	1.29	8.60	91.4	0	白色半透明の溶融物
B-2	15.0	11.1	74.0	26.0	0	無色透明なガラス状溶融物と白色の結晶部分に分相化
B-3	15.0	12.1	80.6	19.4	0	白色のくすんだガラス状の溶融物の表面に結晶析出
B-4	15.0	11.8	78.7	21.3	0	薄黄色透明で良好なガラス
B-5	15.0	2.45	16.3	0	83.7	薄黄色の溶融物とガラス化していない軽石状部分に分相化
B-6	15.0	0	0	0	100	全体が軽石状になり明らかにガラス化しない溶融物
B-7	15.0	10.3	68.7	31.3	0	薄黄色透明なガラス状の溶融物の表面に少量の結晶析出
B-8	15.0	10.5	70.0	30.0	0	薄黄色透明なガラス状の溶融物の表面に少量の結晶析出
B-9	15.0	11.8	78.7	21.3	0	黄色透明の良好なガラス
B-10	15.0	10.3	68.7	31.3	0	黄褐色のガラス状の溶融物の表面に結晶析出
B-11	15.0	0	0	0	100	全体が軽石状になり明らかにガラス化しない溶融物
B-12	15.0	13.1	87.3	12.7	0	無色透明なガラス状部分と白色の結晶部分に分相化
B-13	15.0	11.2	74.7	25.3	0	薄黄色透明なガラス状の溶融物の表面に少量の結晶析出
B-14	15.0	9.59	63.9	36.1	0	黄色透明の良好なガラス
B-15	15.0	11.5	76.7	23.3	0	無色透明の良好なガラス
B-16	15.0	11.8	78.7	21.3	0	黄色透明の良好なガラス
B-17	15.0	10.0	66.7	33.3	0	白褐色の流動性の悪い溶融物
B-18	15.0	11.0	73.3	26.7	0	白褐色の流動性の悪い溶融物
B-19	15.0	11.4	76.0	24.0	0	白褐色の流動性の悪い溶融物
B-20	15.0	10.5	70.0	30.0	0	薄黄色透明なガラス状の溶融物の表面に少量の結晶析出
B-21	15.0	11.2	74.7	25.3	0	薄黄色透明の良好なガラス
B-22	15.0	12.3	82.0	18.0	0	黄色透明の良好なガラス
B-23	15.0	11.8	78.7	21.3	0	黄色透明の良好なガラス
B-24	15.0	11.2	74.7	25.3	0	黄色透明の良好なガラス
B-25	15.0	11.7	78.0	22.0	0	薄黄色透明の良好なガラス
B-26	15.0	11.7	78.0	22.0	0	濃黄色透明の良好なガラス
B-27	15.0	11.8	78.7	21.3	0	白褐色の溶融物
B-28	15.0	11.9	79.3	20.7	0	黄色透明の良好なガラス
B-29	15.0	12.3	82.0	18.0	0	黄色透明の良好なガラス
B-30	15.0	13.2	88.0	12.0	0	黄色透明の良好なガラス
B-31	15.0	12.2	81.3	18.7	0	濃黄色透明の良好なガラス
B-32	15.0	9.11	60.7	0	30.3	黄色のガラス状溶融物と白褐色の結晶部分に分相化

[0016] According to this, a vitrification condition is presented in B-4, B-7 to B-10, B-12 to B-16, B-21 to B-26, and B-28 to B-32, and the range of a brewing presentation is [in B-2 O₃] 0 - 60wt% in ZnO 0 - 60wt% 20 - 80wt% at BaO.

[0017] When the still better glass (amorphous glass) about the presentation shown in Table 1 is chosen, as for BaO, the range of ZnO of B-2 O₃ is 0 - 60wt% 0 - 60wt% 40 - 80wt%.

[0018] 30wt(s)%, 50wt(s)%, B-2 O₃ is 20wt(s)%, and, as for Table 1 and the nonlead glass shown in B-31, ZnO has [BaO] the physicochemical property which was most excellent as alternative sealing material of conventional lead glass.

[0019] Namely, when the nonlead glass shown in B-31 was used for the sealing experiment, it did not generate but sealing and closure were fully possible for the exfoliation and the crack by the stress produced in the sealing section. However, as shown in a table, although it is as high as 480 degrees C to Tg(glass transition point)302 degree C of lead glass, and is as high as 537 degrees C to Tf(softening temperature)320 degree C and sealing temperature is higher than lead glass to Tx(crystal deposit temperature)432 degree C at 590 degrees C and a high point in the thermodynamic

property by X-ray analysis, 110 degrees C and great difference are not to index $T_x - T_g$ 130 degree C of the thermal stability of glass (Table 3).

[0020]

[Table 3]

	T_g (°C)	T_f (°C)	T_x (°C)	$\Delta T = T_x - T_g$	X線分析	析出結晶
鉛ガラス	302	320	432	130	無定形	無し
B-1	同定不可	同定不可	同定不可	同定不可	結晶化	B_2O_3
B-2	(600以上)	(600以上)	(600以上)	同定不可	ほぼ無定形	B_2O_3
B-3	562	578	(600以上)	(38以上)	ほぼ無定形	B_2O_3
B-4	540	565	(600以上)	(60以上)	無定形	無し
B-5	482	503	575	93	ほぼ無定形	ZnO
B-6	同定不可	同定不可	同定不可	同定不可	結晶化	ZnO, BaO
B-7	(600以上)	(600以上)	(600以上)	同定不可	ほぼ無定形	B_2O_3
B-8	564	572	(600以上)	(36以上)	無定形	無し
B-9	530	560	(600以上)	(70以上)	無定形	無し
B-10	465	485	550	85	無定形	無し
B-11	同定不可	同定不可	同定不可	同定不可	結晶化	ZnO, BaO
B-12	565	588	(600以上)	(35以上)	ほぼ無定形	B_2O_3
B-13	550	582	(600以上)	(50以上)	無定形	無し
B-14	570	592	(600以上)	(30以上)	無定形	無し
B-15	557	575	(600以上)	(43以上)	無定形	無し
B-16	535	570	(600以上)	(65以上)	無定形	無し
B-17	445	450	477	32	ほぼ無定形	BaO
B-18	541	571	(600以上)	(59以上)	結晶化	B_2O_3
B-19	564	583	(600以上)	(36以上)	結晶化	B_2O_3
B-20	542	575	(600以上)	(58以上)	ほぼ無定形	B_2O_3
B-21	555	592	(600以上)	(45以上)	無定形	無し
B-22	550	587	(600以上)	(50以上)	無定形	無し
B-23	554	590	(600以上)	(46以上)	無定形	無し
B-24	556	591	(600以上)	(44以上)	無定形	無し
B-25	540	583	(600以上)	(60以上)	無定形	無し
B-26	525	578	(600以上)	(75以上)	無定形	無し
B-27	516	582	(600以上)	(84以上)	結晶化	B_2O_3 , ZnO, BaO
B-28	508	538	592	84	無定形	無し
B-29	500	534	(600以上)	(100以上)	無定形	無し
B-30	485	525	583	98	無定形	無し
B-31	480	537	590	110	無定形	無し
B-32	477	540	(600以上)	(123以上)	ほぼ無定形	BaO

[0021]

[Example] (Example 1 of an experiment)

The reagent chemicals of Wako Pure Chem were used for the 3 boron oxide (B_2O_3) and the zinc oxide (ZnO) which were used as a reagent which forms reagent glass, and the barium oxide (BaO). Other analytical reagents etc. used reagent chemicals similarly.

[0022] The list of the preparation presentations of the raw material metallic oxide

prepared to the preparation table 1 of unleaded low melting glass is shown. What fully mixed the raw material metallic oxide of Table 1 by the predetermined presentation was put into the platinum crucible, and it calcinated for 60 minutes at about 1000 degrees C within the electric furnace. Then, melt was slushed into the alumina boat and the glass rod was created. The stamp mill (ANS143, NITTO KAGAKU) ground the glass rod after cooling in atmospheric air, and the particle size was classified in 100micro or less.

[0023] The point (T_g) of the low melting glass of a unleaded system that measurement preparation of a glass transition point and the softening temperature was carried out transferring [glass], softening temperature (T_f), and crystallization initiation temperature (T_x) were measured using the differential thermal analyzer (DT-40, Shimadzu). All samples are the programming rate of 10 degrees C / min, and performed temperature up measurement to 25-600 degrees C. Alpha-aluminum $2O_3$ was used for the correlation sample (Table 3).

[0024] The coefficient of thermal expansion of the unleaded system low melting glass in which the coefficient of thermal expansion carried out measurement preparation was measured using the apparatus for thermomechanical analysis (TMA8310, physical science electrical-and-electric-equipment incorporated company). That by which the prepared granulated glass was fused again, it fabricated to the 5x5x20mm (vertical x horizontal x height) square pole, and the raised bottom side was fabricated in parallel was used as a test portion. The temperature up was carried out by 5 degrees C / min to 25-200 degrees C, and it asked for the average coefficient of thermal expansion α . Alpha-aluminum $2O_3$ was used for the correlation sample.

[0025] Structural analysis of unleaded system low melting glass by the powder X-ray diffraction method (XRD) which carried out structural-analysis preparation was performed using the powder X-ray plant (Geiger FREX 2013 mold, physical science electrical-and-electric-equipment incorporated company). The scan speed was performed by 2 times / min.

[0026] The schematic diagram of the procedure of the sealing experiment to sealing experiment drawing 1 is shown. Making two sheet glass rival estimated the sealing experiment. Thinner was added to powder-like unleaded system low melting point powder glass, it fully kneaded, and the glass paste was prepared. The electric furnace performed temporary baking during 30 minutes for the sheet glass which applied the prepared glass paste to homogeneity at sheet glass, and applied the glass paste in the glass transition point neighborhood. Then, in piles, it fixed with a clip, the sheet glass which has not applied the glass paste to the sheet glass picked out from the electric furnace was again put into the electric furnace, and this baking (sealing) was performed for 60 minutes under the constant temperature near softening temperature.

[0027] The preparation presentation of the B- $2O_3$ -BaO-ZnO system nonlead glass prepared to Table 1 and Table 2 this time, yield, and its appearance were summarized. It divides into three, glass recovery, a recovery impossibility, and unmelting, about yield. This is because the melting condition of the prepared glass changes in the platinum crucible with presentations of a metallic oxide. The glass to which the metallic oxide of three components reacted good with the burning temperature of 1000 degrees C was glass which was rich in the fluidity. Also in case such glass slushes and collected the glass prepared on the alumina boat, it was about 70% or more of high yield. It is the residue which remained in the platinum crucible that recovery was impossible on the occasion of

recovery. Furthermore, unmelting is not fused at all under burning temperature, but shows the massive pumice-like matter.

[0028] About the appearance of the prepared glass, it is roughly divided into three. the appearance of the typical unleaded system glass -- yellow -- transparent glass (B-31) and a yellowish-white color -- it checked the glass (B-3) which the white crystal deposited on the front face of transparent glass, and was phase-splitting-ized on it, and that did not fuse at all but an appearance changed with the presentations of B-2s O₃, BaO, and ZnO which are pumice-like matter (B-11) a lot (Table 2).

[0029] The result of having identified the vitrification range of B-2O₃-BaO-ZnO system nonlead glass is expressed to drawing 2 using the Misumi Line Fig. < in drawing shows the presentation of the prepared glass. < The value shown below shows the glass transition point of the prepared B-2O₃-BaO-ZnO system nonlead glass. The vitrification range is an inside curve about the range which could collect glass by high yield and the glass transition point has prepared below 600 degrees C, and showed the glass recovery critical range with the outside curve (broken line). The glass with which the presentation of the preparation at the time of preparing glass was rich in the fluidity at the low-melt point point in the range of 20-80wt%B-2 O₃, 0-60wt%ZnO, and 0-60wt%BaO was able to be prepared.

[0030] The temperature curve for which drawing 3 was asked from the glass transition point of the B-2O₃-BaO-ZnO system nonlead glass which was shown all over the Misumi Line Fig., and which was prepared and was prepared by the presentation is shown. The wavy line in drawing is the temperature curve. It asked for the temperature curve from the prepared B-2O₃-BaO-ZnO system nonlead glass to 470-560 degrees C. The temperature curve for which it asked shows that a glass transition point goes up, if the content of B-2 O₃ increases. Then, the effect of B-2O₃ content of B-2O₃-BaO-ZnO system nonlead glass was summarized to drawing 7. Here, two sequences of B-2, 3, 4 and 5, B-7, and 8, 9 and 10 were summarized. When the content of B-2 O₃ increased, the glass transition point was also found by going up on the increment target in monotone.

[0031] Structure evaluation of the prepared B-2O₃-BaO-ZnO system nonlead glass was performed using the powder X-ray diffraction method (XRD). The result is shown in drawing 2. The B-2O₃-BaO-ZnO system nonlead glass prepared [especially] here evaluated whether it is amorphism glass or they were glass ceramics. In order to perform sealing processing, it is desirable that it is amorphism glass. This is because the property change by the heat history is small, so it is possible to change sealing conditions, such as sealing temperature and time amount, freely. Although O in drawing is amorphism glass and ** is amorphism glass fundamentally, it is shown that the glass with which the crystal deposit was checked in part, and x are glass ceramics.

[0032] It checked that the good vitrification range shown in drawing 2 as the continuous line was amorphism glass. The XRD chart of three typical patterns is shown in drawing 5. (a) - in drawing (c) is the XRD chart of the amorphism glass (B-3) containing glass ceramics, crystallization glass (B-11), and amorphism glass (B-31) a part, respectively. When there were many contents of B-2 O₃ like B-3, the result in which the crystal of B-2 O₃ deposits in part was obtained. The melt which cannot be vitrified at all like B-11 has checked the crystal pattern of each oxide. And observing the crystal pattern of each metallic oxide of what has been vitrified very good like B-31 was not completed at all.

[0033] Usually, the lead glass currently generally widely used as sealing glass is

amorphism glass which has a XRD pattern like B-31. From the result of drawing 2, a low-melt point point, amorphism, and the range where good glass is obtained were able to be identified. Especially, B-10 in the Misumi Line Fig., and 30 and 31 have engine performance sufficient as sealing glass of a unleaded system.

[0034] Identification of the metallic oxide which is effective in lowering a glass transition point is also more possible than the vitrification range shown as the continuous line of drawing 2. Since the dissociation energy and the coordination number per mol were the same as that of it of PbO, ZnO which are some configuration metallic oxides of nonlead glass was expected as an alternative metallic oxide of PbO.

[0035] However, the reduction in a glass transition point was unobservable with the increment in ZnO. ZnO considered as a mesh modifier oxide functions as a mesh formation oxide rather than it functions as a content increasing as a mesh modifier oxide. On the other hand, the glass transition point was able to be decreased by the increment in the content of BaO.

[0036] In B-2O₃-BaO-ZnO system nonlead glass, a metallic oxide like BaO with metaled large atomic weight has the large contribution as an alternative metallic oxide of PbO. That is, BaO embellishes the network structure with the form where an oxygen bridge is cut in the glass which makes B-2 O₃ the network structure, and is decreasing the polymerization degree of the network structure.

[0037] The effect of the content of BaO of B-2O₃-BaO-ZnO system nonlead glass is shown in drawing 6. Here, the addition effectiveness of BaO was summarized about two sequences, 30 B-2O₃-xBaO-(70-x) ZnO and 40 B-2O₃-xBaO-(60-x) ZnO. When the content of BaO increased both sequences, it has checked that a glass transition point decreased. It turned out that the direction of the sequence of 30 B-2O₃-xBaO-(70-x) ZnO whose content of B-2 O₃ is 30wt(s)% has the large contribution as a mesh modifier oxide of BaO, and has caused a sharp reduction of a glass transition point with the increment in the content.

[0038] Here, reference is made about sealing of the B-2O₃-BaO-ZnO system nonlead glass prepared this time, and a closure performance evaluation. Elements indispensable to sealing and a closure property are the coefficient of thermal expansion of sealing glass, and the stability of the sealing glass in a sealing process.

[0039] Since glass is an ingredient which is easy to break, it needs to fit the coefficient of thermal expansion of glass and a sealing-ed object, needs to control the stress (stress) of the sealing section, and needs to use it as a firm sealing object.

[0040] Then, as for sealing material, it is desirable that it is as low a coefficient of thermal expansion as possible. In the coefficient-of-thermal-expansion measurement using the apparatus for thermomechanical analysis (TMA) of nonlead glass (B-31), the result of about 50×10^{-6} to 6×10^{-6} degree C⁻¹ has been obtained here. The lead glass currently generally used is about 100×10^{-6} to 6×10^{-6} degree C⁻¹, and the nonlead glass prepared this time was understood that a coefficient of thermal expansion is quite low.

[0041] It is mixing the ceramic filler of a low expansion coefficient, in order that especially the lead glass that is general sealing material may make this coefficient of thermal expansion low, and using this as sealing material in most cases. Since the B-2O₃-BaO-ZnO system nonlead glass prepared this time does not add a ceramic filler specially but ** also fully has the low-fever expansion coefficient, practical added value is high.

[0042] Furthermore, what summarized the thermal property of B-2O₃-BaO-ZnO system

nonlead glass etc. to Table 3 and drawing 4 is shown. T_x (crystallization initiation temperature) - T_g (glass transition point) of front Naka serves as an index of the thermal stability of glass. It is shown that glass is more stable as this value is large. The value of $T_x - T_g = 110$ degree C in especially B-31 was acquired. This value was a value near $T_x - T_g$ ($T_x - T_g = 130$ degree C) of the lead glass which is the sealing material currently generally used. It becomes clear that the B-2O₃-BaO-ZnO system nonlead glass prepared by the presentation of B-31 this time is glass which has stability equivalent to lead glass.

[0043] Therefore, B-31 which has all the indispensable conditions of a low-melt point point, amorphism, low-thermal expansion, and thermal stability was used for the sealing experiment. In the result of having evaluated sealing of B-2O₃-BaO-ZnO system nonlead glass (B-31), and a closure property by making two sheet glass rivaling in drawing 1, neither exfoliation nor a crack was generated with the stress produced in the sealing section. Therefore, also when it was used for actual flat-surface fluorescence tubing, confidentiality has fully been held.

[0044] The glass forming region which is shown in drawing 8 instead of B-2 O₃ as a mesh formation oxide (NWF) according to the non-plumbic acid ghost of the V₂O₅-ZnO-BaO system using V₂O₅ is obtained. V₂O₅ 30 - 70wt%, (Example 2 of an experiment) ZnO set 0 - 50wt%, BaO set to 50 - 80wt%, amorphism glass was obtained, and the result that less than [crystal deposit temperature T_x 500 degree C], a glass transition point T_g , and softening temperature T_f were 400 degrees C or less as shown in Table 4 was obtained (drawing 9).

[0045]

[Table 4]

	T _g (℃)	T _f (℃)	T _x (℃)	ΔT = T _x - T _g	X線分析	析出結晶
鉛ガラス	302	320	432	130	無定形	無し
V-1	同定不可	同定不可	同定不可	同定不可	結晶化	V ₂ O ₅
V-2	同定不可	同定不可	同定不可	同定不可	結晶化	
V-3	同定不可	同定不可	同定不可	同定不可	結晶化	
V-4	345	380	435	90	無定形	無し
V-5	同定不可	同定不可	同定不可	同定不可	結晶化	
V-6	回収不可	回収不可	回収不可	回収不可	—	—
V-7	370	380	500	130	ほぼ無定形	
V-8	265	310	370	105	無定形	無し
V-9	320	335	420	100	無定形	無し
V-10	同定不可	同定不可	同定不可	同定不可	結晶化	
V-11	回収不可	回収不可	回収不可	回収不可	—	—
V-12	同定不可	同定不可	同定不可	同定不可	結晶化	
V-13	370	415	450	80	無定形	無し
V-14	355	385	430	75	無定形	無し
V-15	同定不可	同定不可	同定不可	同定不可	結晶化	
V-16	270	310	325	55	無定形	無し
V-17	回収不可	回収不可	回収不可	回収不可	—	—
V-18	同定不可	同定不可	同定不可	同定不可	結晶化	
V-19	265	285	315	50	ほぼ無定形	
V-20	260	290	320	60	無定形	無し
V-21	380	410	435	55	結晶化	
V-22	330	355	375	45	ほぼ無定形	
V-23	260	275	295	35	無定形	無し
V-24	330	380	420	90	無定形	無し
V-25	220	230	320	100	結晶化	
V-26	330	315	380	50	無定形	無し
V-27	320	345	405	85	結晶化	
V-28	回収不可	回収不可	回収不可	回収不可	回収不可	—
V-29	回収不可	回収不可	回収不可	回収不可	回収不可	—
V-30	回収不可	回収不可	回収不可	回収不可	回収不可	—
V-31	回収不可	回収不可	回収不可	回収不可	回収不可	—
V-32	回収不可	回収不可	回収不可	回収不可	回収不可	
V-33	回収不可	回収不可	回収不可	回収不可	回収不可	—
V-34	340	380	395	55	ほぼ無定形	V ₂ O ₅

[0046] As opposed to the above-mentioned nonlead glass (B-31) or 1 weight section of V2O5 (Example 3 of an experiment) When the 4th component Bi 2O3 and TeO2 are prepared, as shown in Table 5, the nonlead glass of a vitreous state with an appearance fluidity good [all] is obtained, and although low melting glass with it was obtained, softening temperature Tf [a glass transition point Tg as low as 371 degrees C and 366 degrees C or] [as 411 degrees C and 410 degrees C] [as low] In the case of the 4th component Bi 2O3, Tx was suitable, and 229 degrees C or more and high glass good to sealing processing were obtained for thermal stability **T.

[0047]

[Table 5]

	B ₂ O ₃	ZnO	BaO	PbO	Bi ₂ O ₃	TeO ₂	T _g (°C)	T _f (°C)	T _x (°C)	ΔT(°C)	ガラス状態
B-31:Pb 1:0.3	(23.0769) 30 (3.0009)	(15.3846) 20 (2.0012)	(38.4615) 50 (5.0034)	(23.0769) +30 (3.0048)	—	—	437 503	475 528	560	123 57	◎
B-31:Pb 1:0.8	(16.6666) 30 (3.0040)	(11.1111) 20 (2.0011)	(27.7777) 50 (5.0031)	(44.4444) +80 (8.0020)	—	—	368 434	417 453	487	119 53	◎
B-31:Bi 1:2	(10.0) 30 (3.0030)	(6.6666) 20 (2.0026)	(16.6666) 50 (5.0038)	—	(66.6666) +200 (20.0026)	—	371	411	600以上	229以上	◎
B-31:Te 1:2	(10.0) 30 (3.0030)	(6.6666) 20 (2.0033)	(16.6666) 50 (5.0027)	—	(66.6666) +200 (20.0026)	—	366	410	524 560	158 194	◎

◎ ; 外観・流動性良好

○ ; 外観or流動性が良好

△ ; 非常に流動性が悪い

x ; 結晶化

[0048] In order to make the coefficient of thermal expansion of the above-mentioned unleaded system low melting glass the same as the coefficient of thermal expansion of a sealing-ed object, and in order to raise the reinforcement of a sealing object, addition mixing of the refractories filler is carried out at the above-mentioned low melting glass.

[0049] As refractories filler powder, there are a KOJIE light, beta and you chestnut PUTATO, beta-spodumene, zircon, an alumina, a mullite, a silica, beta-quartz solid solution, silicic-acid zinc, aluminum titanate, etc.

[0050] The mixed approach of low-melting-glass powder and refractories filler powder is very good in what kind of approach. In case a grinder grinds the low-melt point point glass block prepared and built, refractories filler powder may be added, and grinding and mixing may be performed. Moreover, to the particle size of arbitration, a refractories filler may be added after grinding low melting glass, it may mix, and you may use.

[0051] (Example 4 of an experiment) In order to consider as a desired coefficient of thermal expansion, alpha and an alumina were mixed as a refractories filler to V-8 in Table 4. Refractories filler powder was put in at a mixed rate shown in Table 6, and it asked for stabilization index **T of glass transition point T_g, softening temperature T_f, and glass. The system (V-8-b) which mixed the refractories filler was excellent in thermal stability as compared with the system (V-8-a) which does not mix a refractories filler, and the low-fever expansion property was acquired. According to the thermal-expansion property of a sealing-ed object, good sealing becomes possible by carrying out optimum dose mixing of the refractories filler.

[0052]

[Table 6]

ガラス	混合比 (V ₂ O ₅ :Al ₂ O ₃)	T _g (°C)	T _f (°C)	T _x (°C)	ΔT(°C)	熱膨張係数 (X10 ⁻⁷ /°C)	流動性
V-8-a	10:0	265	310	370	105	101.9	◎
V-8-b	9:1	260	310	400	140	91.8	◎

◎ : 流動特性良好

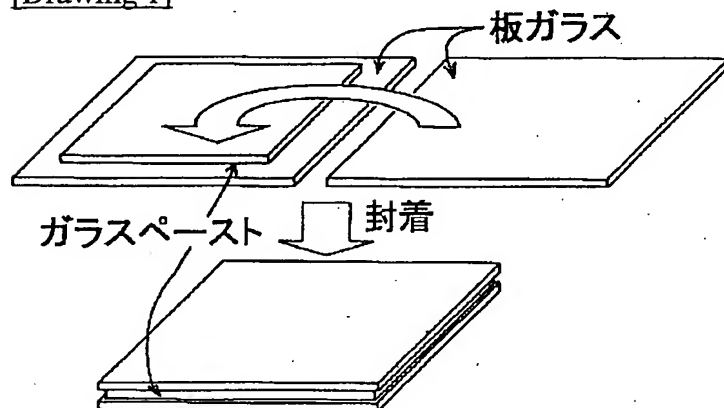
[0053]

[Effect of the Invention] Since this invention was constituted as mentioned above, it can

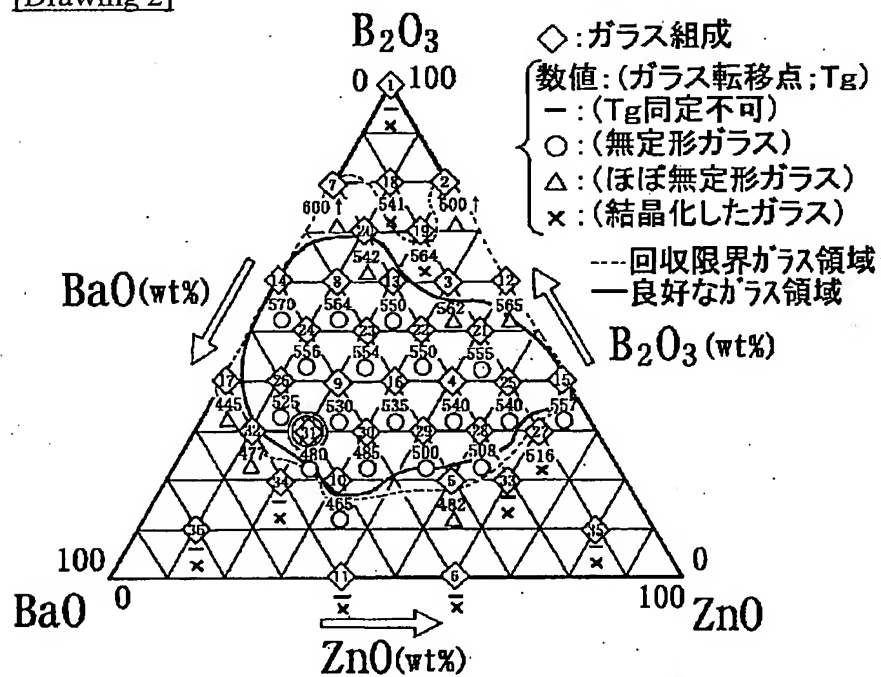
obtain the unleaded system low melting glass for sealing processing which matched and was excellent in lead system low melting glass.

DRAWINGS

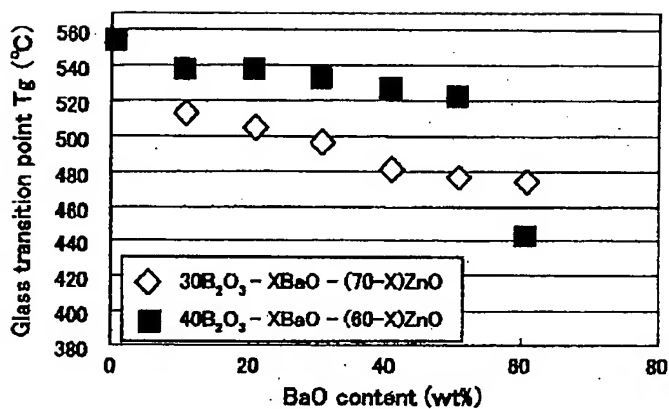
[Drawing 1]



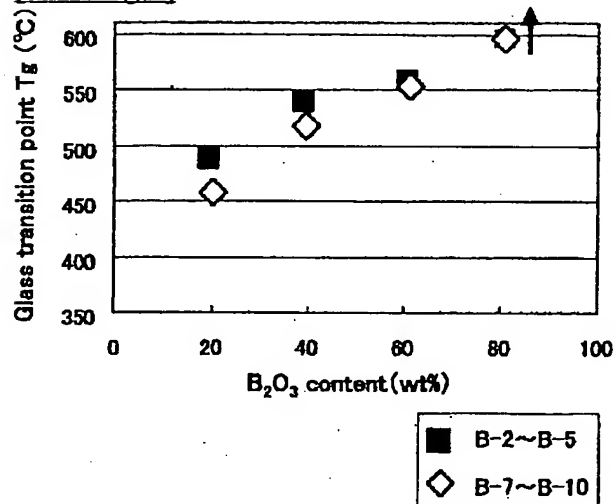
[Drawing 2]



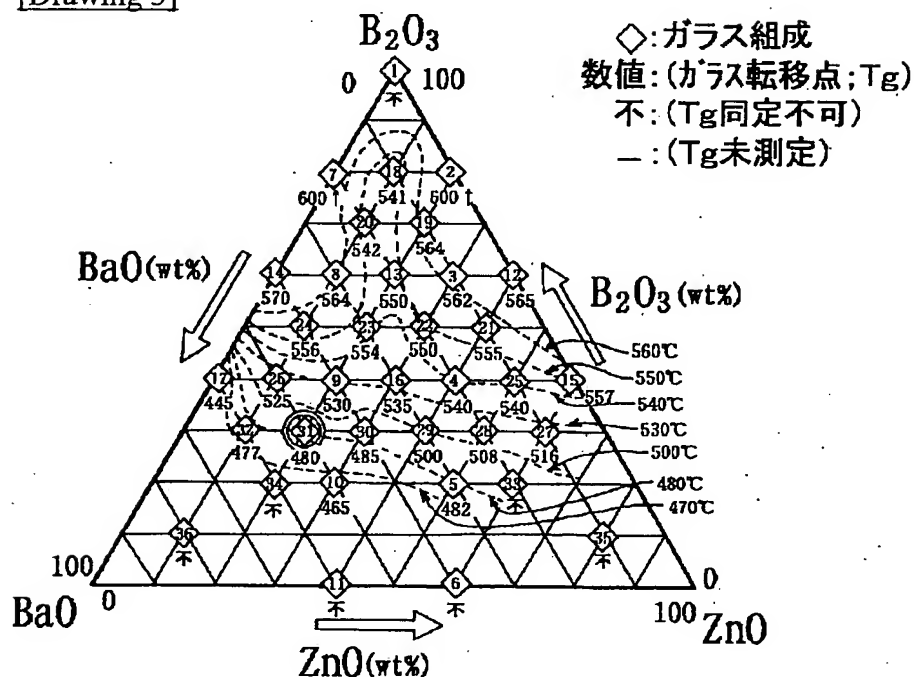
[Drawing 6]



[Drawing 7]

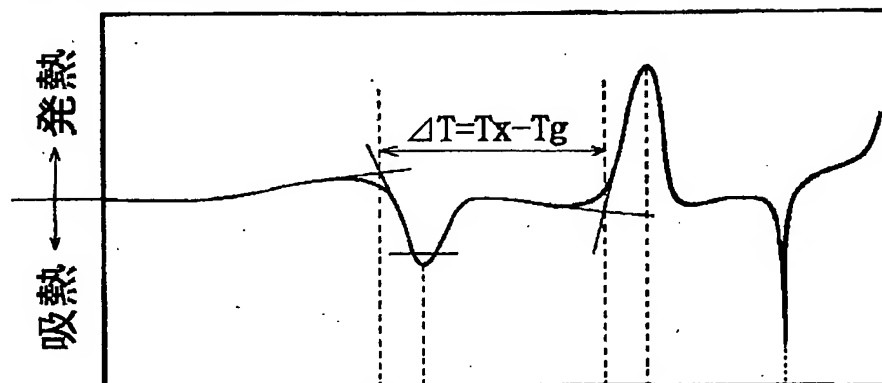


[Drawing 3]



[Drawing 4]

示差熱分析装置 (DTA) による測定

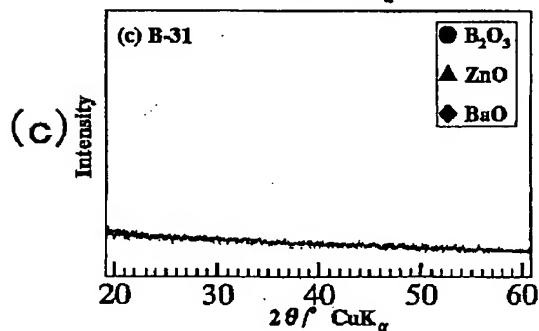
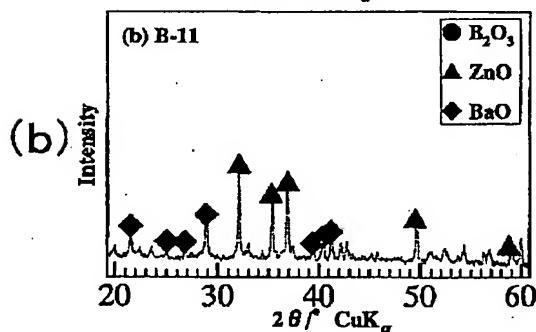
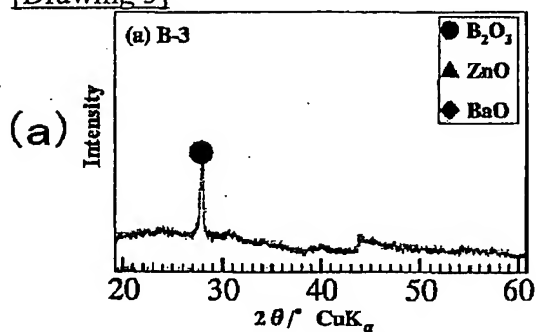


Tg Tf Tx

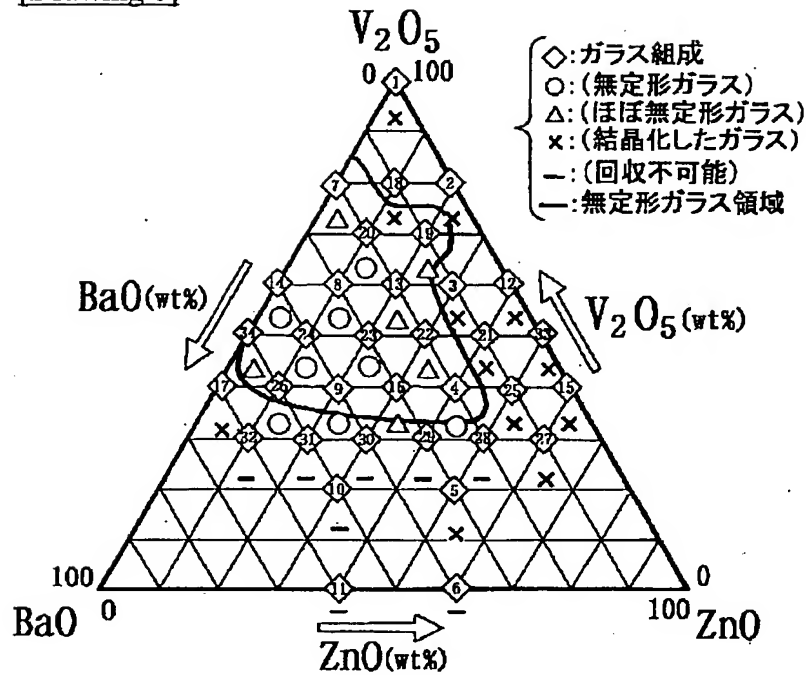
温度 (°C)

Tg : ガラス転移点
Tf : 軟化点
Tx : 結晶析出温度

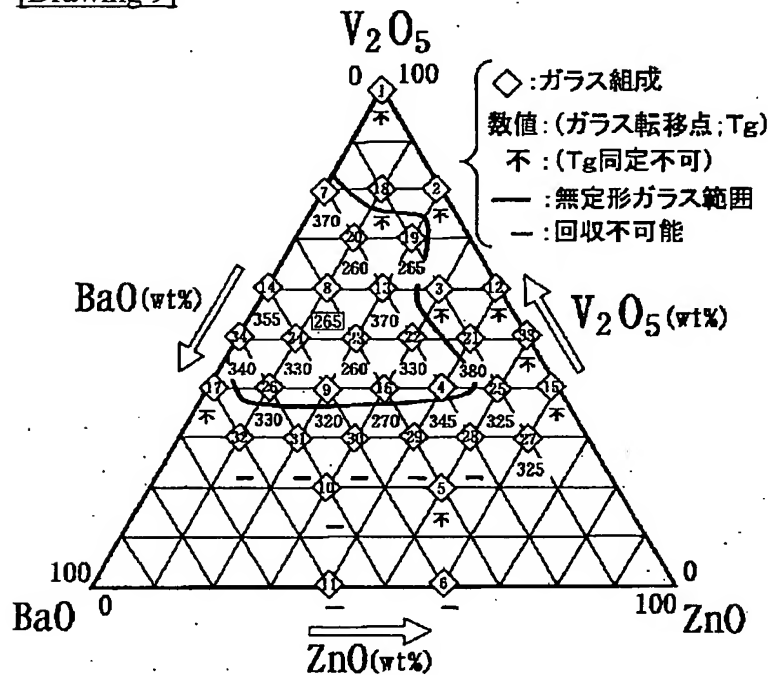
[Drawing 5]



[Drawing 8]



[Drawing 9]



[Claim(s)]

[Claim 1] Unleaded low melting glass for sealing processing which is the unleaded system constituent which consists of a mesh formation oxide, an intermediate oxide, and a mesh modifier oxide, prepares weight % of these oxides and comes to select the low-

melt point point matter of glassiness.

[Claim 2] Unleaded [a mesh formation oxide / B-2 O₃ or V₂O₅, and an intermediate oxide / ZnO and a mesh modifier oxide] low melting glass for sealing processing according to claim 1 which constituted the unleaded system constituent by BaO.

[Claim 3] Unleaded low melting glass for sealing processing according to claim 1 to 2 which prepared BaO 0 - 60wt% 20 - 80wt%, and prepared ZnO for B-2 O₃ which constitutes the above-mentioned unleaded system constituent in the range of 0 - 60wt%.

[Claim 4] Unleaded [B-2 O₃ which constitutes the above-mentioned unleaded system constituent] low melting glass for sealing processing according to claim 1 to 3 which BaO prepared 50wt(s)% 30wt(s)% and ZnO prepared to 20wt(s)%.

[Claim 5] Unleaded [V₂O₅ which constitute the above-mentioned unleaded system constituent / 30 - 70wt% and ZnO] low melting glass for sealing processing according to claim 1 or 2 0 - 50wt% and whose BaO are 50 - 80wt%.

[Claim 6] Unleaded low melting glass for sealing processing according to claim 1 to 5 which carried out addition preparation of Bi₂O₃ to the above-mentioned unleaded system constituent.

[Claim 7] Unleaded low melting glass for sealing processing according to claim 1 to 5 which carried out addition preparation of TeO₂ to the above-mentioned unleaded system constituent.

[Claim 8] Unleaded low melting glass for sealing processing according to claim 1 to 7 which mixed the refractories filler.